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WATER SOFTENING BY FILTRATION THROUGH ARTIFICIAL ZEOLITE[1]

By Daniel D. Jackson

As rain falls to the ground, it is, of course, soft water, but as it comes in contact with the earth's surface and particularly if it percolates through the soil, it becomes hardened by dissolving compounds of lime and magnesia. The extent of this hardening depends upon the nature of the soil and the time of contact.

These salts of lime and magnesia are detrimental to many manufacturing processes; produce scale and corrosion in boilers, and render the water less suitable for drinking and general domestic use.

The method which has been most extensively used for softening water is that of treatment in large tanks with solutions of caustic lime and soda ash. The lime and soda precipitate the greater part of the hardening compounds in the water which settle to the bottom of the tanks and are from time to time drawn off and disposed of. This process involves the use of tanks which take up a considerable amount of space; the more or less constant attention of a man for the feeding and regulation of chemicals, and the necessity of the disposal of considerable amounts of sludge.

These difficulties are done away with in the new process, which involves the simple filtration of the hard water through a bed of artificial zeolite. The discovery of this new process was made by Prof. Robert Gans, Director of Chemistry of the German Geological Survey. It was through an investigation of the bodies in the soil and their properties which are utilized for the purpose of fertilization that the exchange value of zeolites was discovered.

As far back as the middle of the last century, Way[2] published statements to the effect that the fertilizing properties of the soil were of a purely chemical nature, taking place in the presence of silicates with the power of exchange of bases in the soil. Leibig[3] opposed this theory. Later on experiments by Lemberg,[4] Eichhorn,[5] Peters,[6] and others showed that natural zeolites exchange their bases for other bases contained in solution in contact with them.

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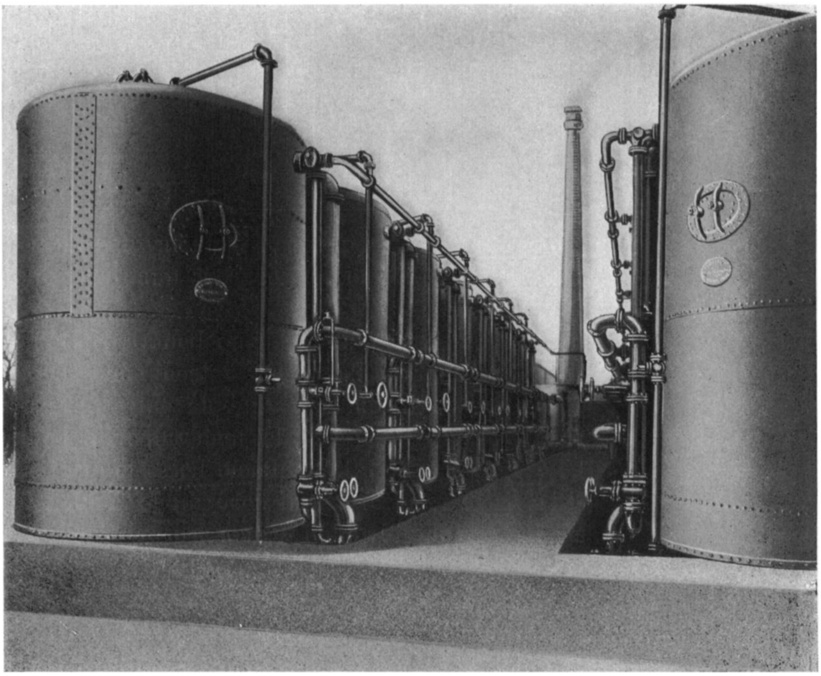
[1] Read and discussed at the Cincinnati convention May, 1915.

[2] *Journ. Agric. Soc. England*, 1850 and 1852.

[3] *Leibig's Annalen*, 1856.

The manufacture of artificial zeolites to prove theories was often attempted but the products obtained were either of a gelatinous, slimy character or of a hard, glassy structure with a small degree of exchange. With the exception of Rumpler,[7] who tried the use of silicates in the sugar industry but without success, nobody had previously attempted to use them for technical purposes.



MUNICIPAL WATER SOFTENING PLANT, HOOTEN, ENGLAND

It remained for Professor Gans[8] to thoroughly investigate the whole subject of the exchange value of soils; to collect and analyze

[4] *Zeitschrift der Deutschen Geologischen Gesellschaft,* 1870, 76, 77, 83 & 87.

[5] *Poggendorf's Annalen,* 1858, pages 105 and 126.

[6] *Landwirtschaftliche Versuchs stationen,* Bd. 2, page 113.

[7] *Die Deutsche Zuckerindustire, 1901, and Internationaler Congress fur angewandte Chemie,* 1903, Bd. III, pages 59 and 69.

[8] *Jahrbuch der Kgl. preussischen Geologischen Landesanstalt,* 1905 and 1906.

all the various zeolites and determine which had the highest exchange value, and finally to produce an artificial zeolite having much greater and more rapid exchange than those found in nature and also of pronounced physical toughness so that it might be successfully used for technical purposes. His attention was first drawn to the subject by noting that waters originally hard would become completely softened by passing through certain soils of volcanic origin, whereupon he investigated thoroughly the chemical nature of these soils and found them to be zeolites of more or less similar composition. He found also that some soils were very much more active than others and by studying these he developed an artificial compound having a formula which would give a very high softening effect. This led to the manufacture of an artificial zeolite through which water could be filtered as through a sand filter.

If a water containing lime and magnesia is passed through such a filter of zeolite of a composition of sodium-alumino-silicate, the sodium will be replaced by the lime and magnesia and the reaction will be the equivalent of what takes place in the old water softening process, except that the water is softened to the zero point, due to the absolute insolubility of the lime and magnesia zeolites formed in the filter.

By the use of this insoluble filtering material as a reagent, it is possible to employ a large excess of this reagent so that the removal of the undesirable bases from the liquid to be treated takes place automatically in the cold, and completely without having any excess of sodium salts in the effluent which is a decided advantage over earlier known methods of softening.

In order to form the ideal zeolite of minutely porous but strong structure, Dr. Gans melted together in a furnace the necessary mineral ingredients consisting of soda ash, feldspar, kaolin and pearl ash in the proper proportions, and the glass thus formed was heated with hot water, lixiviated, washed and sieved to the proper size. This material when used in a filter of the proper mechanical type and run at suitable rates had the power of removing all lime and magnesia from any type of water so that the effluent water would be absolutely zero in hardness. The size and rate of the filter depend upon the amount of water used and the hardness which it contains. The usual depth of filter is from 3 to 4 feet and the usual rate from 10 to 15 feet per hour when the hardness is from 10 to 20 degrees.

In the earlier lime soda process a reaction time of at least four hours is needed if a reduction of the hardness down to from 3 to 6 degrees is desired, and only a small excess of reagents in the effluent is allowed. By the zeolite process a reaction time of about two minutes for soft water; of three to six minutes for medium hard water and of seven to twelve minutes for a very hard water is needed to remove *all* of the hardness.

In this process the calcium and magnesium of the water exchange places with the sodium of the zeolite giving a sodium salt in solution in the treated water as shown by the following formulae:

Sodium zeolite + calcium salts = calcium zeolite + sodium salts
$Na_2O\cdot Al_2O_3\cdot 2SiO_2 + CaCO_3 = CaO\cdot Al_2O_3\cdot 2SiO_2 + Na_2CO_3$
$Na_2O\cdot Al_2O_3\cdot 2SiO_2 + CaSO_4 = CaO\cdot Al_2O_3\cdot 2SiO_2 + Na_2SO_4$
$Na_2O\cdot Al_2O_3\cdot 2SiO_2 + Ca(NO_3)_2 = CaO\cdot Al_2O_3\cdot 2SiO_2 + 2NaNO_3$
$Na2O\cdot Al_2O_3\cdot 2Sio_2 + CaCl_2 = CaO\cdot Al_2O_3\cdot 2SiO_2 + 2NaCl$

Similar reactions also take place when magnesium salts form the second half of the equation instead of lime salts.

When the point is reached where the sodium of the zeolite has become sufficiently exhausted so that the reaction does not take place completely, then the filter is stopped and regenerated by running in an 8 per cent solution of common salt and allowing it to stand for about eight hours, when the following reaction takes place:

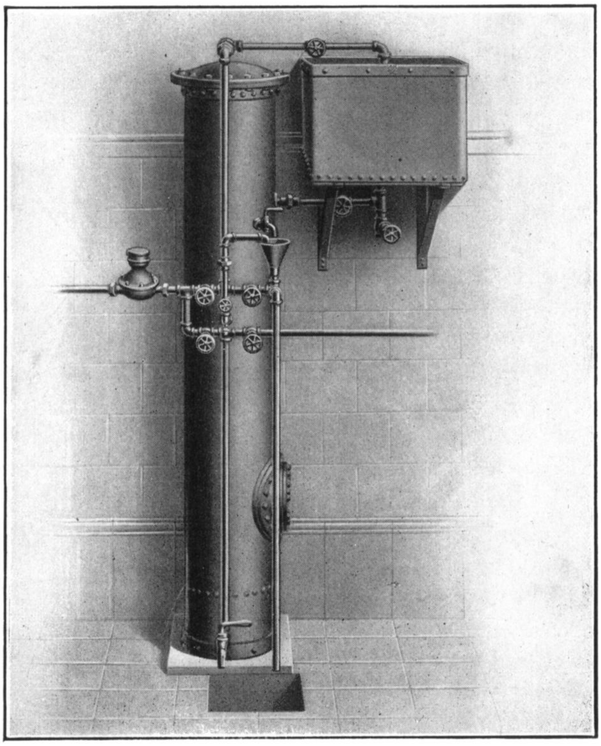
Calcium zeolite + common salt = sodium zeolite + calcium chloride
$CaO\cdot Al_2O_3\cdot 2SiO_2 + 2NaCl = Na_2O\cdot Al_2O_3\cdot 2SiO_2 + CaCl_2$

By this mass reaction of the common salt the zeolite is changed to its original composition. The salt solution containing the soluble lime and magnesium salts is then run off and the filter washed when it is again ready for use.

It is apparent that the filter will require little attention as there will be no shifting or changing of the proportion of the reagents due to fluctuations in hardness. The sodium of the salt goes back into place in the zeolite and the clear solution when run off contains all the lime and magnesia as soluble chlorides which may be run into any drain. The filter, after washing, is then ready for a second run.

This process may be kept up indefinitely with but slight losses of zeolite. The municipal laundries in Berlin had been running a filter for four years when inspected in 1912 and no replacements of zeolite had been made during that time, while the capacity had in no way diminished. Waters very high in organic matter may require a certain percentage yearly replacement.

The whole series of alumino-silicates may be made from sodium alumino-silicate by simple replacements of the bases in various soluble salts and there are oxidizing, reducing and catalizing compounds which may be used for various purposes. The one most in use at the present time is manganese zeolite or permutit, which when treated with permanganate of potash makes a compound of high oxidizing value and is used for making filters for the removal of iron and manganese from water. Such filters have been extensively installed abroad, the largest ones are in Dresden, Germany, for the removal of manganese from the municipal supply, and in Hooten, England, for the elimination of iron from the water supply



Household Water Softening Plant

of that town. At Hooten also is the municipal water softening plant.

The process also lends itself readily to small installations as it requires so little attention and may be employed in pressure filters which avoid an installation built high in the air or double pumping.

The cost of operation is the cost of common salt used which is from $2 to $8 a ton, depending upon the locality. If the water is five degrees in hardness then the cost is usually about 1 cent per thousand gallons.

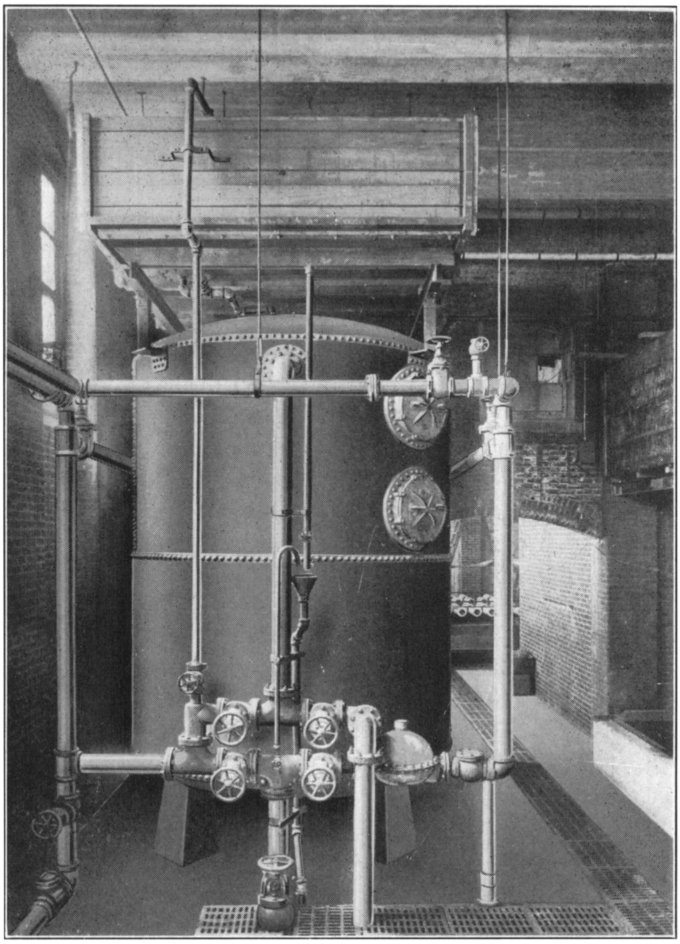
In the household, water filtered through artificial zeolite is smooth and velvety for bathing, shaving and shampooing, and prevents rough skin and chapped hands. In the laundry it reduced the soap bills and prevents the muddiness which often comes from the precipitation of lime and magnesium soaps on the white goods. In the boiler it prevents scale and corrosion. The boiling time of vegetables is shortened and in some cases the flavor improved. Vegetables like peas are softer and less pulpy.

For drinking purposes it has been found that water softened in this manner gave much greater and more rapid digestibility of food than when softened by the lime soda process. This is undoubtedly due to the presence of bicarbonates which increase digestive action.

In the textile industries and public laundries the process is extensively used due to the saving of soap and the improvement in the quality and clearness of the goods. Even when moderately hard waters are used soap compounds which are impossible to remove may form small deposits on the surface of materials. In dyeing these deposits cause spots or blemishes or unevenness so that the general effect of the color is not as clear and bright as it should be and if the water fluctuates in hardness it is extremely difficult to match shades.

The Bradford woolcombers of England informed the writer on his visit there that the water filtered through zeolite rendered the wool softer and gave a larger percentage of the higher grades than when the water was softened by the lime soda process. The installation was smaller and required much less attention and always reduced the water to zero hardness which in this work was found to be of great importance.

The process has been in commercial use in Germany since 1908 and in the United States since 1911. It has been most extensively installed for the treatment of water for industrial purposes or for boiler use, but some municipal plants have been constructed, notably at Hooten, England, where a water of 20 degrees of hardness is reduced to 10 degrees by treating one half of the supply consisting of one million and a quarter gallons, and mixing the zero water obtained with the other half to produce a water of 10 degrees of hardness.



Factory Water Softening Plant

DISCUSSION

Mr. Edward Wegmann: The speaker was always under the impression that soft water was best for health; but in reading descriptions of water works built in England, the engineers there state positively that in towns where they have hard water the people live longer than where they have soft water. That is contrary to what has been the speaker's conception. What do you think about that statement? A man prominent in engineering published that as a positive fact.

Mr. Daniel D. Jackson: Someone has said that statistics are for the purpose of proving something that is not so; and it would seem in this case the statistics you refer to are chargeable with that imputation. The speaker believes, although of course there are all sorts of opinions, that it is much better to drink soft water. Certainly the lime salts in the waters which are drunk are not utilized physiologically as far as is known. Even if they were, there is probably more lime in a glass of milk than in several buckets of water; so that rickets and other things which have been attributed to soft water are practically eliminated from consideration. It is not probable that anything of that kind can be brought about by the use of soft water. One of the author's children was given only distilled water until he was six years old. He is now playing on football and baseball teams and so far he has broken no bones.

A Member: Why is pearlash used in the preparation of zeolite; why is it added?

Mr. Daniel D. Jackson: A very small amount of pearlash is added to make the mixture fuse at a little lower point, just as it happens in the case of materials in a chemical crucible. By the addition of potash feldspar and high heat you can get along without any pearlash at all.

A Member: Did you say that you use 8 per cent of salt solution in regenerating zeolite, and that it removes the calcium and magnesium taken up by the gravel? Is there a waste of salt in that process, or is there a way of recovering the salt, or separating it from the chlorides of magnesium and calcium?

Mr. Daniel D. Jackson: If you have a reaction in chemistry, in order to get the reverse action you must have a very large excess of material, so an eight per cent salt solution is used for the purpose of getting what is called a mass reaction. In that case the sodium will go back into the zeolite again, and the calcium will come out as chlorides of lime and magnesia. As to being able to recover the salt, in some hotels where it is employed, the salt solution is used for a seabath, but it is so cheap that it would not be practical to recover it from the lime and magnesia to be used over again in the filter.

Mr. Edward Bartow: The Illinois State Water Survey has been interested for several years in the Permutit process. When the first publications appeared we purchased a small plant and tested it quite thoroughly in our laboratory. It was found that water could be obtained with zero hardness. Last summer, through the courtesy of the Permutit Company in Germany and the United States Softeners Company in England, several plants including some which Mr. Jackson has mentioned were visited. One or two of our observations may be of interest.

At a plant of the General Electric Company near Berlin, Germany, they used zeolite to soften the water to make tea. This company furnishes bottled tea to its employees, and the ordinary water did not give a sufficiently clear product. By use of the zeolite process to soften the water they got a perfectly clear, acceptable tea. In Bradford, England, the plant of the Woolcombers Limited has a combination lime, soda and zeolite plant, one of the largest installations, probably, in the manufacturing establishments. They use a water of 30 degrees hardness, 30 grains per imperial gallon, that is softened to the greatest extent possible with lime and soda, and then the hardness reduced to zero with zeolite. It was stated that the workmen using the water in the plant could immediately tell the difference between the water softened to zero by the zeolite process and water from the city supply, which had a hardness of only three or four grains per gallon. They reported a saving of two pounds of soap for each grain of hardness removed. In this country, a zeolite plant was put in in a little textile factory where they had used soap to soften the water; avoiding the use of any chemical for fear of injuring the goods. It was calculated that they would be able to save $2 per thousand gallons because of the amount of soap that would be saved. After they tried the zeolite softened water they reported that the saving was $3 per thousand gallons as against the cost with the raw water. Of course a similar saving would have been made by softening the water in any way. This is just an illustration of what the possibilities are. Lime, soda and zeolite go well together. The combination is most often used in England.

MR. DANIEL D. JACKSON: In one place in Germany they were making tea for a very large factory where there were 3000 employees, and work was stopped at noon that they might have their tea or their beer. The amount of tea that was originally used with hard water was just twice what they had to use after they had recourse to soft water; in other words, the essential oils in the tea were used up to a very large extent by the lime and magnesia in the water, but when the tea was made with soft water this did not take place, and they only had to use half the amount of tea. In this large concern that made quite a difference. Undoubtedly such a result as that might occur with oils of other character, possibly in tobacco and other materials which may be treated with water. Those are ideas which are yet to be developed.

A MEMBER: Is soft water as palatable as hard water?

MR. DANIEL D. JACKSON: If you have been used to drinking very hard water, and then change to soft water, you will not like it; and vice versa; but once you are accustomed to drinking soft water, it is very much better for you.

A MEMBER: Why not use the natural deposits that you spoke about instead of the artificial?

MR. DANIEL D. JACKSON: Because the percentage of exchange in the natural deposits which we know about is small as compared with the artificial material which is made up theoretically correct. In Germany some of these compounds have been used which were made and purified from zeolite stone; but you have a filter three or four times larger, and the results are not nearly as good, so that that method is hardly practicable.

A MEMBER: Has zeolite softened water been used very extensively as boiler feed water, and what results were thereby obtained?

Mr. Daniel D. Jackson: There are hundreds of installations for boiler purposes in this country and all through the north of England, and particularly in Germany; and the result of using this water is that you do not get any scale whatever, you have clean iron with no scale and little or no corrosion. That is because the magnesia combined with chlorides and nitrates which produced the highest degree of corrosion are removed. When these are taken out of the water the corrosion is eliminated, so that you have a great saving in boiler operation.

A Member: What effect is there on the foaming quality of the water?

Mr. Daniel D. Jackson: If a water has something like fifty degrees of hardness, as it has in some places, the foaming will be a material detriment in that supply. If you have water which foams originally in the boiler, it will still foam when you soften it; in other words, softening the water does not reduce the foaming characteristics.